

AD-A132 397

DIFFUSION AND SORPTION OF CYCLOHEXANE VAPOR IN SBS AND  
SBR COPOLYMERS(U) CALIFORNIA UNIV BERKELEY DEPT OF  
ELECTRICAL ENGINEERING G T CANEBA ET AL. 30 AUG 83  
TR-4 N00014-81-K-0516

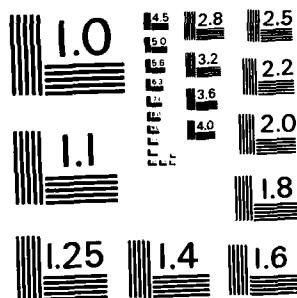
1/1

UNCLASSIFIED

F/G 11/9

NL


END  
PAGE  
FOOTED  
9 83  
DT #



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

ADA 132397

DTIC FILE COPY

12

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0516

TECHNICAL REPORT NO. 4

Diffusion and Sorption of Cyclohexane  
Vapor in SBS and SBR Copolymers

by

Gerald T. Caneba, David S. Soong and John M. Prausnitz

Prepared for Publication

in the

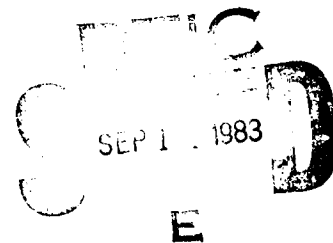
Journal of Macromolecular Science, Physics Ed.

Department of Chemical Engineering  
University of California, Berkeley,  
Berkeley, CA 94720

August 30, 1983

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited



83 09 14 014

Diffusion and Sorption of Cyclohexane

Vapor in SBS and SBR Copolymers

by

G.T. Caneba, D.S. Soong, and J.M. Prausnitz

Department of Chemical Engineering  
University of California, Berkeley  
Berkeley, California 94720

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Availability for Special
A	



#### ABSTRACT

Diffusion and sorption of cyclohexane vapor in styrene-butadiene copolymers were used to study the morphology of an SBS triblock copolymer (29.3 wt % styrene) cast from different solvents. The weight gain or loss of this SBS and several SBR (5, 23, 45 and 85 wt % S content) samples were continuously monitored at 40°C and at penetrant pressures of 30, 60, 90 and 120 torr. Significant differences exist in the equilibrium sorption among the different samples. Possible reasons for this observation are explored. The one corroborated by dynamic mechanical measurements attributes the differences to varying interphase volume fractions. The interphase region separating the PB and PS phases in SBS was assumed to be a continuous profile of equivalent SBR with different S contents. Experimental results, coupled with simple calculations, indicated that the overall interphase volume fraction in the SBS are 0.28 for the MEK/THF-cast (1:9 volume ratio of MEK and THF) sample, 0.15 for the toluene-cast sample, and 0.04 for the cyclohexane-cast sample. Important observations consistent with these results are: (a) the existence of a relative minimum (at around 20-30 wt % S content) in the plot of the equilibrium sorption of cyclohexane vs. S content in rubbery SBR; and, (b) a relative maximum in the plot of the mutual diffusion coefficient of cyclohexane in SBR vs. the concentration of cyclohexane in SBR.

## INTRODUCTION

Diffusion and sorption of small molecules into polymeric matrices have been used to study the morphology of structured polymers. For example, Illers [1] and Gray and Gilbert [2] studied the effects of heat treatment on structural order in polyvinyl chloride through changes in solvent sorption behavior. Kapur and Rogers [3] used diffusion of inert gases to investigate the influence of aging on quenched polypropylene films. Blackadder and Vincent [4] investigated the morphology of slowly cooled and quenched polypropylene films by sorption measurements. These latter authors also used sorption to examine the influence of drawing on the structure of polyethylene terephthalate [4].

In recent years, much attention has been devoted to the structure of block copolymers, particularly styrene-butadiene-styrene (SBS) triblock copolymers. The degree of mixing and state of aggregation in such a mixed-polymer system is determined by the Gibbs energy of mixing. The very small entropy gain from mixing macromolecules and the usually positive enthalpy of mixing produce a net positive Gibbs energy, leading to immiscibility and phase separation [5,6]. However, in block copolymers, such as SBS, the size of the component blocks and the presence of chemical linkages between blocks limit phase separation to a microscopic scale (on the order of molecular dimensions), often called microphase separation [5]. It is this heterogeneous structure that provides SBS with many desirable engineering properties [5].

Thermodynamic studies and physical experiments (electron microscopy, thermal analysis, dynamic mechanical measurements) on microphase separation of block copolymers [7-12] have dealt primarily with the gross two-phase microstructure of the pure blocks. However, experimental results of dynamic mechanical measurements and thermal analyses obtained by Miyamoto [13] as well as Beecher [14] suggest the existence of a significant interphase layer separating the pure blocks. More recent theories also recognize the existence of an interphase region [15-18]. With the use of data obtained from dynamic mechanical measurements of SBS cast from different solvents, Diamant [19] developed a computer model to infer the overall size and composition profile of the interphase. These studies suggest that the overall interphase volume fractions can be significant, ranging from 0.04 to 0.66 [19]. Hashimoto et al. [20] used SAXS technique to determine the interphase thickness of SI directly [20,21] and confirmed the concept of diffuse interphase.

In this work, experiments on diffusion and sorption of cyclohexane vapor into SBS block copolymers have been performed to ascertain the influence of network morphology on the relevant transport and thermodynamic properties, including the effect of size and composition profile of the interphase. Since the interphase can be treated as a continuous distribution of styrene-butadiene random copolymers (SBR), each with average composition corresponding to the local composition profile of the interphase, experiments have also been performed on SBR samples to determine the equilibrium

sorption and transport properties of these systems.

The triblock copolymer used in this work has a relatively low overall styrene (S) content. This promotes the penetration of cyclohexane into the copolymer, as cyclohexane is a good solvent for PB but a poor one for PS. Sorption and desorption runs can be completed within reasonable experimental time scales.

Diffusion data on SBS copolymers have been reported in the literature [22-26]. For sorption of cyclohexane vapor into SBS with 27 weight % S content, Sefton and coworkers [22-24] observed pseudo-Fickian sorption behavior with the absence of length-scaling, a condition in which the sorption curve appears to be Fickian but does not reduce to a single curve for different sample thicknesses. They attributed such non-Fickian behavior to time-dependent diffusivities and concluded the existence of a significant interphase region in SBS. Odani and coworkers [25,26] also offered the same explanation in their studies of n-hexane sorption into various SBS samples. The same authors reported equilibrium solubilities of n-hexane in the copolymers and PB homopolymer. They found that if the copolymers were assumed to have a sharp interphase, then, for a fixed penetrant activity, the pure PB domains should have a higher equilibrium n-hexane concentration than that of the PB homopolymer. Hence, the assumption of sharp interphase led to different equilibrium solubilities of PB in the block copolymer as compared to the homopolymer, an intriguing



result.

Our experimental data, coupled with simple calculations, not only clarify the above-mentioned findings (with the pseudo-Fickian behavior observed by Sefton and coworkers [22-24]) for the existence of a significant interphase region, but also link this region to the equilibrium solubility results of Odani et al. [26]. In addition, our results support the conclusions reached by Diamant [19] concerning the overall size and composition profile of the interphase for SBS samples cast from different solvents.

## EXPERIMENTAL

Sample Preparation

The SBS sample, TR-41-1648, was provided by Shell Development Company. SBR samples (5,23,45 and 85 weight percent styrene, with molecular weights ranging from 200,000 to 300,000) were purchased from Scientific Polymer Products, Inc. Table 1 lists some important specifications and structural information for these samples. SBR and SBS samples were essentially pure, except for 1.25% stabilizer added to the SBR sample with 5% (by weight) S content.

Appropriate amounts of SBS sample were dissolved (about 9% by weight) in each of the following solvents: cyclohexane (a good solvent for PB but a poor one for PS); toluene (a neutral solvent between PS and PB); and a 9:1 volume mixture of tetrahydrofuran (THF) and methylethyl ketone (MEK) (a good solvent for PS but a poor one for PB). The SBR samples were dissolved in toluene. The solutions were filtered to remove solid contaminants that may have been present in the original samples. Samples were prepared as sheets by spincasting from the filtered solutions. The sheets were subsequently dried to constant weight at 60°C in a vacuum oven. The dried SBS and glassy SBR samples were then annealed at 110°C for about one hour in vacuum to remove internal stresses. TR-41-1648 SBS samples prepared in this manner had detailed morphology depending on the casting solvent [27], while the SBR samples were homogeneous.

For sorption and desorption studies, samples ranging

from 0.2 to 0.4 mm in thickness were cut into sheets with typical areas of 2 cm x 1 cm. For density measurements, samples with areas as small as 0.5 cm x 0.5 cm were used. Density data, sample weights and sample areas (determined with a micrometer) were used to estimate sample thickness. The thickness was accurate to  $\pm 0.001$  mm (i.e., less than 0.5% error).

#### Apparatus and Procedure

To study sorption and desorption characteristics of cyclohexane in SBS and SBR, the weight gained or lost was measured as a function of time. The results are plotted as  $M_t/M_\infty$  vs.  $t^{1/2}/l$ ; where  $M_t$  is the weight change (gain or loss) at time  $t$ ,  $M_\infty$  is the total weight change at equilibrium and  $l$  is the sample thickness.

Figure 1 shows a schematic diagram of the diffusion apparatus. A Cahn RG automatic electrobalance was used to monitor the weight change. The assembly was enclosed in a constant-temperature chamber controlled to within  $\pm 0.3^\circ\text{C}$  of the setpoint. Cyclohexane vapor from a liquid penetrant source was introduced into the system. This penetrant source was immersed in a constant-temperature bath kept to within  $\pm 0.1^\circ\text{C}$  of the setpoint temperature. To operate the system at pressures lower than the vapor pressure of the penetrant liquid, a pressure controller (manostat diver) was used. Adjustments in the setpoint pressure were facilitated by a pressure transducer, which also allowed pressure to be

continuously monitored on a strip-chart recorder. Tubes and valves used for penetrant transport were made of glass and kept at the temperature of the chamber containing the electrobalance assembly. For metal connections, glass-metal welded couplings were used while rubber connections were used only where flexibility was needed and in lines where leaks could be tolerated. Instead of using a strip-chart recorder to monitor the weight change from the electrobalance, data were stored on a PET computer via an analog-digital converter for subsequent transfer onto floppy disks.

Before starting a sorption run, the system was completely sealed and evacuated. Then the pressure controller was set and penetrant vapor admitted into the electrobalance. In the course of a run, analog electrical signals corresponding to weight changes were amplified, digitized and stored onto floppy disks for data reduction and analysis.

Upon completion of the sorption run, the penetrant was evacuated from the electrobalance to begin the desorption run. This was accomplished by simultaneously closing the penetrant-source valve and opening the pump and ballast tank valves. The large capacity of the ballast tank generated a rapid drop in system pressure. The evacuation process could therefore be treated as instantaneous for data analysis of weight loss. Weight change was similarly recorded as a function of time on the disks for subsequent data analysis.

## RESULTS AND DISCUSSION

Sorption Isotherm

Figure 2 shows the sorption isotherms for SBR at 40°C. The quantities  $P$  and  $P_0$  are the pressure and the saturated pressure of cyclohexane at 40°C (184 torr). These curves are concave upward, indicating enhanced dissolution of the penetrant in SBR at high pressures. In addition, the curve for the 23% (by weight) S content is lower than that for 5% (by weight) S content, while the plot for the 45% (by weight) S content is higher than that for 23% (by weight) S content. Sorption isotherm of the SBR sample with 85% (weight) S content is not shown, because it sorbs a negligible amount of the penetrant within the normal experimental time scales (30 min to 2 hr).

To facilitate comparison of these results to those for SBS, Figure 3 shows a plot of the equilibrium sorption vs. the overall S content of the SBR and SBS. With the use of Fox equation [28] for the glass-transition temperature of a random copolymer, the glassy and rubbery regions (as a function of S content in SBR at 40°C) were determined from the  $T_g$  values of the component homopolymers (-90° and 100°C for PB and PS, respectively). At this temperature, the corresponding SBR composition marking the transition from the rubbery to glassy region is 81.5% (by weight) S content. In the rubbery region, SBR exhibits a relative minimum of equilibrium sorption for all penetrant pressures used. Although no polymer-solution theory is

capable of predicting this behavior, we will note that the same type of curve (with a minimum) for the equilibrium sorption of hydrogen and deuterium gases [29] and rare gases [30] has been observed experimentally for SBS with different overall S contents. In addition, minima shown in Figure 3 and in the above-mentioned papers [29,30] consistently occur around 20-30% (by weight) S content.

The points for the SBS samples are plotted along 29.3% (by weight) S content, the overall S content of TR-41-1648. These three points correspond to the equilibrium sorption values (at 40°C and 60 torr) of samples cast from cyclohexane, toluene and MEK/THF. Note that these SBS samples sorb more penetrant than SBR of comparable S contents. Furthermore, differences exist in the equilibrium sorption values among the SBS samples: the MEK/THF-cast sample sorbs the most (9.38 mg/100 mg dry sample), followed by the toluene-cast sample (8.90 mg/100 mg dry sample), and finally, the cyclohexane-cast sample (8.50 mg/100 mg dry sample). If we assume a sharp interphase and impermeable PS domains, then the PB domains should sorb 13.27 mg/100-mg dry MEK/THF-cast sample, 12.59 mg/100-mg dry toluene-cast sample, and 12.02 mg/100-mg dry cyclohexane-cast sample. Clearly, these values are all greater than the extrapolated equilibrium sorption value for pure PB, about 11.5 mg/100 mg dry sample (Figure 3). Assumption of microphase-separated morphology with a sharp interphase apparently leads to the above observation which is difficult to resolve. We will thus use the sharp interphase concept as a reference for comparison with results

expected for morphologies with diffuse interphase. Since the SBS has a phase-separated network morphology, sorption of penetrant may induce deformation of the domain structure, causing strain of the phases. This suggests a possible explanation to account for the observed enhanced uptake and the differences in equilibrium sorption among the different samples. If we assume the rubbery phase swells upon cyclohexane penetration, the elastic network may sustain significant strain energy which elevates the chemical potential of the sorbed cyclohexane (31,32). This increased chemical potential will hinder further sorption of cyclohexane. For lamellar morphology, a net reduction of 6-10% of equilibrium sorption is estimated based on the analysis of Meier (32) considering both intradomain (loop) and interdomain (bridges) contributions. For other morphologies, however, the percent reduction would be less (31). In this estimation, the elastomeric blocks are assumed to be in an entangled state with 6000 as the molecular weight between adjacent entanglements. The calculated reduction in equilibrium sorption, however, contradicts our experimental observation of enhanced sorption. Hence, network swelling is not a major factor in promoting sorption. It is possible to rationalize that the test samples may be originally in a state of compression. This compressed state is not completely relieved despite the annealing treatment at 110°C for one hour. Subsequent cyclohexane penetration will thus relieve this compressive strain and sorption will be promoted. However, the trapped elastic strain is expected to be highest for the cyclohexane-cast sample. Since cyclohexane is poor solvent for PS, the PS rigid phase will be formed first, while cyclohexane gradually leaves the PB phase

during casting. The MEK/THF-cast sample has PS dissolved in the solvent until later stages of casting. It would thus be difficult to trap in elastic deformation during casting. We must then conclude that the cyclohexane-cast sample should exhibit higher sorption than the MEK/THF-cast sample. This again contradicts experimental observations. Another possible explanation is that the PS phase may craze, creating additional sorption sites. However, the experimental time scale to approach equilibrium sorption indicates involvement of rubbery phase only. A third interpretation relies on interphase sorption to account for the observed sorption enhancement.

As indicated by Odani et al. [26], these differences in the equilibrium sorption values of PB homopolymer and of the

PB blocks in SBS (with assumed sharp interphase) suggest the existence of a diffuse boundary in the block copolymers. Since SBR samples with high S contents sorb more penetrant than the PB homopolymer, SBS samples with significant interphase regions are able to pick up more penetrant than those with sharp interphases. The calculation below further substantiates this statement.

#### Evaluation of the Overall Interphase Volume Fraction in SBS

From the density data in Table 1 and the curves in Figure 3, the interphase volume fraction in the SBS samples can be determined with the following assumptions:

1. The penetrant sorbs only into the rubbery portions of the SBS samples. These include part of the interphase.



2. The transition from the rubbery to the glassy portions of SBS occurs at 81.5% (by weight) S content, i.e., somewhere in the interphase. This point remains independent of penetrant sorption, as the glassy portion of the interphase is assumed impermeable to the diffusant within the experimental time scale.
3. The interphase composition profile is linear and the SBS morphology is lamellar, i.e., boundary curvature effect is neglected. This assumption is not absolutely necessary. However, it greatly simplifies the calculation and is made here for convenience.
4. The component volumes comprising the SBS samples are additive.

These assumptions permit ready determination of the overall interphase volume fractions for each of the SBS samples. Inputs for the calculation include the density data in Table 1 (for assumption 4) and the equilibrium sorption data for the SBS and SBR samples at 60 torr and 40°C (used in conjunction with assumptions 1,2,3 and 5). The calculated interphase volume fractions of SBS are: (a) 0.28 for the MEK/THF-cast sample, (b) 0.15 for the toluene-cast sample, and (c) 0.06 for the cyclohexane-cast sample. These values are in reasonable agreement with Diamant's work [19], where he reported volume fractions of 0.10 for the MEK/THF-cast sample and 0.04 for the cyclohexane-cast sample.

### Sorption and Desorption Behavior

Figures 4 and 5 show the integral sorption and desorption curves for the diffusion of cyclohexane in SBR and SBS at 40°C and penetrant activity of 60 torr. Sorption and desorption behavior for SBR with 5% (by weight) S content and for cyclohexane-cast SBS are similar; they support the above calculations indicating the near absence of the diffuse interphase in the cyclohexane-cast SBS sample. Since most of the sorbed penetrant is in the PB phase, its sorption and desorption behavior should be similar to that of <sup>SBR with</sup> 5% (by weight) S content. The effect of this relatively narrow interphase on the diffusion behavior in the cyclohexane-cast SBS sample is insignificant. Figure 4 shows that for SBR, sorption curves are above the desorption curves and that the difference between these curves increases with S content of the SBR samples. If this trend persists for SBR samples of S contents higher than 45% (by weight), the gap between the sorption and desorption curves should also increase for SBS samples with increasing interphase volume fractions. This is consistent with SBR species of high S content sorbing much more penetrant than their low S-content counterparts. The middle plot of Figure 5 shows that for the toluene-cast SBS sample (interphase volume fraction = 0.15), the sorption curve is significantly higher than the desorption curve; more so than the gap between the corresponding curves for the cyclohexane-cast sample (interphase volume fraction = 0.06). However, in

the bottom plot of Figure 5 the difference between the sorption and desorption curves for the MEK/THF-cast sample (interphase volume fraction = 0.28) is smaller than that for the toluene-cast sample. In fact, the sorption and desorption curves for the MEK/THF-cast sample intersect at long times. Based on the diffuse-interphase model for SBS, the only explanation for this unusual behavior is the possibility of a reversal in the trend of the sorption/desorption behavior of SBR at S contents higher than 45% (by weight), i.e., for SBR with increasing S content the gap between the sorption and desorption curves starts to decrease until these curves exchange positions. This reversal in the positions of the sorption and desorption curves implies the existence of a relative maximum in the diffusivity-concentration plots of these SBR species at a concentration below the equilibrium sorption [33].

Figure 6 shows the integral sorption curves of SBR samples at 60 torr and 40°C. Note that the diffusivity decreases with S content. This trend is consistent with the fact that as the S content of SBR increases, its free-volume decreases. Thus, the intrinsic mobility of the penetrant decreases.

The same type of plot for the SBS samples at the same penetrant activity and temperature is shown in Figure 7. The following observations are noted:

1. In the interval  $0 \leq M_t/M_\infty \leq 0.2$ , the sorption curves converge at the same line, indicating Fickian behavior with the same initial diffusivity.
2. For  $M_t/M_\infty > 0.2$ , the sorption curves diverge first and eventually converge as  $M_t/M_\infty \rightarrow 1$ .  
In the region where deviations occur, the MEK/THF-cast sample sorbs penetrant at the slowest rate, while the cyclohexane-cast sample sorbs penetrant at the fastest rate.

Since the penetrant diffuses much faster in the PB phase than in the interphase, at the start of the sorption run no difference in the sorption behavior exists among the SBS samples. As the diffusant begins to enter into the interphase, deviations in the sorption curves occur. At the time when much of the penetrant is still sorbed in the PB phase of the cyclohexane-cast sample, a large fraction of the sorbed penetrant is already in the interphase region of the MEK/THF-cast sample. Because the interphase is able to sorb more penetrant than the PB phase, and because the penetrant has a lower mobility in the interphase, the sample with the largest interphase region (MEK/THF-cast sample) has the slowest sorption rate as indeed observed experimentally.

When all the rubbery regions of the SBS samples are saturated with the penetrant, the sorption rate drops to almost zero. Some sorption in the glassy region still persists. However, in the experimental time scale of 30 min to 2 hr, changes in the weight readings are barely detectable; sorption in the glassy regions can be neglected for all practical purposes.

Evaluation of Mutual Diffusion Coefficients of  
Cyclohexane in the SBR Samples

Integral sorption and desorption data can be used to determine the diffusivity of cyclohexane in SBR at penetrant concentrations prevailing at the start and end of the sorption and desorption runs, where the penetrant concentration profile is essentially flat. Nonlinear Regression [34] was applied to the solution of Fick's second law of diffusion to compute the diffusivity from the experimental sorption and desorption curves at  $M_t/M_\infty > 0.95$ .

The results of these calculations, shown in Figure 8, indicate the existence of a relative maximum in the diffusivity-concentration curves of SBR samples with 5 and 23% (weight) S content and possibly SBR samples of higher S contents. For the diffusion of vapors into rubbery polymers, relative maxima in the D-C curves are common because diffusivity is the product of a mobility factor and a thermodynamic factor [35]. The mobility factor increases with penetrant concentration, whereas the thermodynamic factor usually decreases. Since a relative maximum in the D-C curve can reverse the positions of the sorption and desorption curves [33], the above explanation entailing the diffuse-interphase concept for the positions of the sorption and desorption curves in Figure 5 is consistent with this experimental finding.

SBR with low S content is found to exhibit Fickian diffusion, but sorption of cyclohexane into rubbery SBR near its glass-transition temperature often exhibits non-Fickian behavior. Since the latter type of SBR sorbs more penetrant than the former, we can attribute the pseudo-Fickian behavior observed by Sefton and coworkers [23-25] to the rubbery portion of the interphase with compositions near the glassy region. With a diffuse interphase for the SBS samples, it is also possible to attribute the observed non-Fickian behavior to that portion of the interphase exhibiting Fickian behavior. At a given time during the sorption process, a concentration profile is established in the PB-rich phase. At the same time, the penetrant diffuses from this medium to the interphase. Since cyclohexane diffuses faster in the PB matrix than in the interphase, the penetrant continues to diffuse into the interphase even after the PB phase is almost saturated. For a thick film, sorption of cyclohexane throughout the sample requires a longer time than in a thin one. Thus, for a given penetrant concentration profile in the PB phase, there is more penetration of cyclohexane into the interphase of a thick sample than that of a thin one. Therefore, length-scaled sorption curves (weight gain vs.  $t^{1/2}/l$ ) for SBS will appear to be faster for a thick sample than for a thin one. For a sharp interphase, the above explanations for the non-Fickian behavior observed in SBS can never be invoked, because cyclohexane diffusion in PB is Fickian and PS is relatively impermeable to vapor transport.

### CONCLUSION

Using sorption and diffusion data, we have shown that in SBS the interphase region is significant; its volume fraction depends on the casting solvent. By describing this interphase region as a continuous profile of SBR, results of vapor sorption experiments of cyclohexane in SBS and SBR yield interphase volume fractions of: (a) 0.28 for the MEK/THF-cast sample, (b) 0.15 for the toluene-cast sample, and (c) 0.06 for the cyclohexane-cast sample.

Minima occur at around 20-30% (by weight) S content in plots of the equilibrium sorption values of cyclohexane vs. styrene content in the rubbery SBR samples. Also, relative maxima exist in plots of the mutual diffusion coefficient vs. concentration of cyclohexane in SBR. For SBS samples, the relative positions of the sorption and desorption curves are generally dependent on their overall interphase volume fractions. As the overall interphase volume fraction rises, the gap between these curves (with the sorption curve higher than the desorption curve) first increases, and then decreases until the sorption and desorption curves cross. These observations are consistent with the above-mentioned results for the overall interphase volume fractions of SBS.

## ACKNOWLEDGMENT

This project was supported by the Office of Naval Research.  
The authors appreciate the help of Dr. David Hansen of the Shell  
Development Company in providing the block copolymer.



## REFERENCES

1. K.H. Illers, Makromol. Chem., 127, 1, (1969).
2. S. Gray and M. Gilbert, Polymer, 16, 387 (1975).
3. S. Kapur and C.E. Rogers, J. Polym. Sci. A-2, 10, 2107, (1972).
4. D.A. Blackadder and P.I. Vincent, Polymer, 15, 2, (1974).
5. M. Shen and H. Kawai, AIChE J., 24, 1 (1978).
6. J.A. Manson and L.H. Sperling, "Polymer Blends and Composites," Plenum, New York (1976).
7. D.J. Meier, J. Polym. Sci., C26, 81 (1969).
8. S. Krause, J. Polym. Sci. A-2, 7, 249 (1969);  
Macromolecules, 3, 84 (1970).
9. V. Bianchi, E. Pedemonte and A. Torturro, J. Polym. Sci., B7, 785 (1969).
10. L. Marker, J. Polym. Preprints, 10, 524 (1969).
11. D.G. LeGrand, J. Polym. Preprints, 11, 434 (1970).
12. T. Inoue, T. Soen, T. Hashimoto and H. Kawai, J. Polym. Sci. A-2, 7, 1283 (1970); Macromolecules, 3, 87, (1970).
13. T. Miyamoto, K. Kodama and K. Shibayama, J. Polym. Sci., Polym. Phys. Ed., 8, 2095 (1970).
14. L. Beecher, L. Marker, D.R. Bradford and J. Aggarwal, J. Polym. Sci., Polym. Symp., 26, 117 (1969).
15. D.F. Leary and M.C. Williams, J. Polym. Sci., B8, 335 (1970).

16. D.F. Leary and M.C. Williams, J. Polym. Sci., Polym. Phys. Ed., 11, 345 (1973); *ibid.*, 12, 265 (1974).
17. E. Helfand and Z.R. Wasserman, Polym. Eng. Sci., 17, 582 (1977).
18. D.J. Meier, ACS, Polym. Preprints, 15, 171 (1974).
19. J. Diamant, Ph.D. Thesis, University of California, Berkeley, 1982.
20. T. Hashimoto, M. Shibayama and H. Kawai, Macromolecules, 13, 1237 (1980).
21. T. Hashimoto, M. Fujimura and H. Kawai, Macromolecules, 13, 1660 (1980).
22. M.V. Sefton and E.W. Merrill, J. Polym. Sci., Chem. Ed., 14, 1581 (1976).
23. M.V. Sefton and E.W. Merrill, 14, 1829 (1976).
24. K.T. Chang and M.V. Sefton, J. Polym. Sci., Polym. Phys. Ed., 15, 1927 (1977).
25. H. Odani, K. Taira, N. Nemoto and M. Kurata, Polym. Preprints, 18, 239 (1977).
26. H. Odani, M. Uchikura, K. Taira and M. Kurata, J. Macromol. Sci.-Phys. B17, 337 (1980).
27. J. Diamant, D.S. Soong and M.C. Williams, Polym. Eng. Sci., 22, 673 (1982).
28. T.G. Fox, Bull. Am. Phys. Soc., 1, 123 (1956).
29. H. Odani, K. Taira, N. Nemoto and M. Kurata, Polym. Eng. Sci., 17, 527 (1977).
30. M. Mehta and M. Dole, Macromolecules, 15, 376 (1982).
31. D.J. Meier, Appl. Polym. Symp. 124, 67 (1974).
32. D.J. Meier, J. Macromol. Sci., Phys., B17, 181 (1980).

33. J. Crank and M.E. Henry, Trans. Faraday Soc., 45, 636 (1949).
34. H.O. Hartley, Technometrics, 3, 269 (1961).
35. G. Rehage, O. Ernst and J. Fuhrmann, Discuss. Faraday Soc., 49, 208 (1970).

Table 1. Composition and Molecular Specifications  
for the Test Samples

SBS, TR-41-1648 (29.3 wt % PS):

MW of the Blocks

$M_{S1}$	16,000
$M_B^*$	78,000
$M_{S2}$	16,000
$M$	110,000

SBR:

<u>Weight Percent Styrene</u>	<u>Density**, g/cm<sup>3</sup></u>
5	0.8888
23	0.9125
45	0.9478
85	1.0212

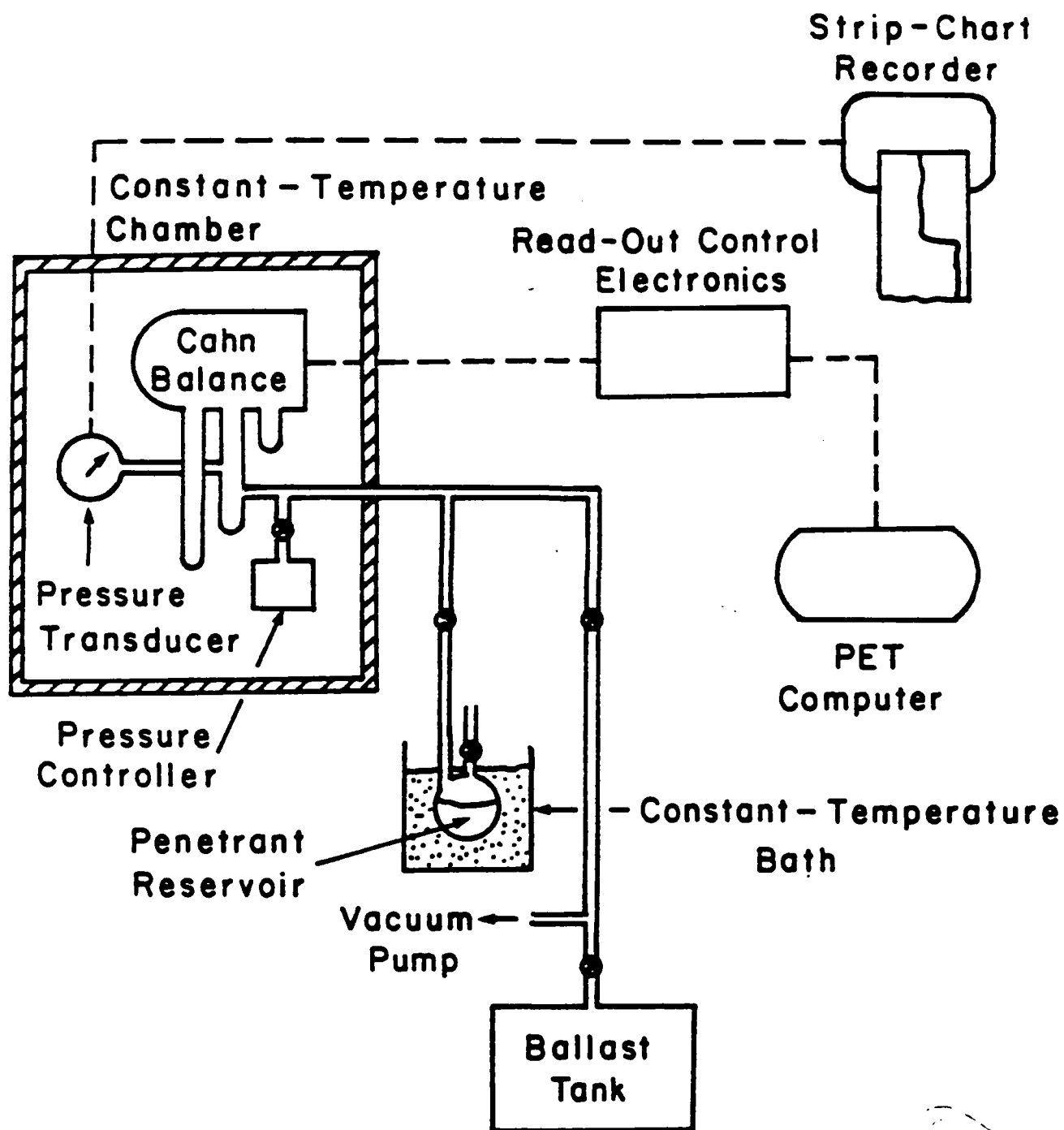
\*Polybutadiene Microstructure

cis 1,4	40%
trans 1,4	50%
trans 1,2	10%

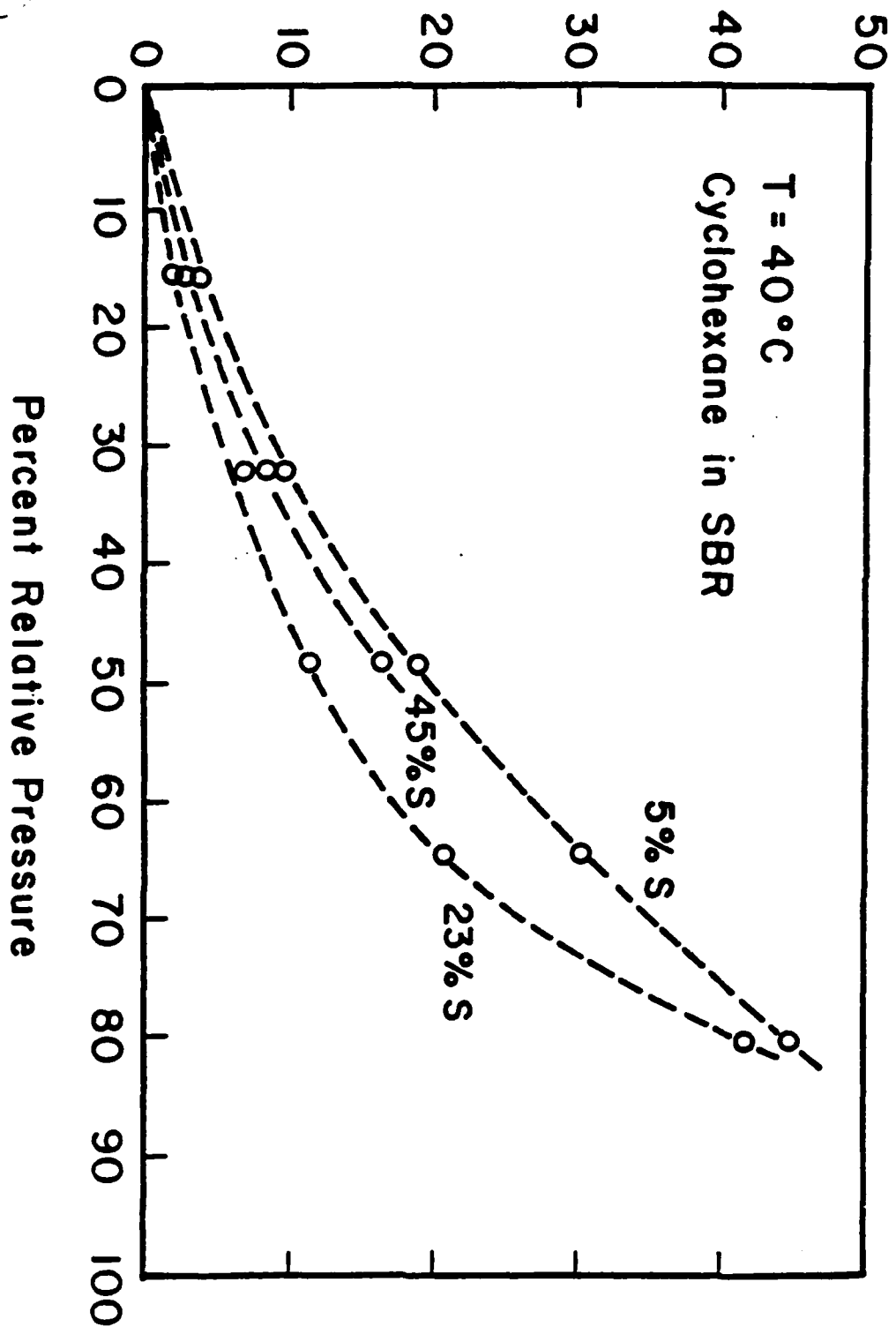
\*\*Measured at 40°C.

## FIGURE CAPTIONS

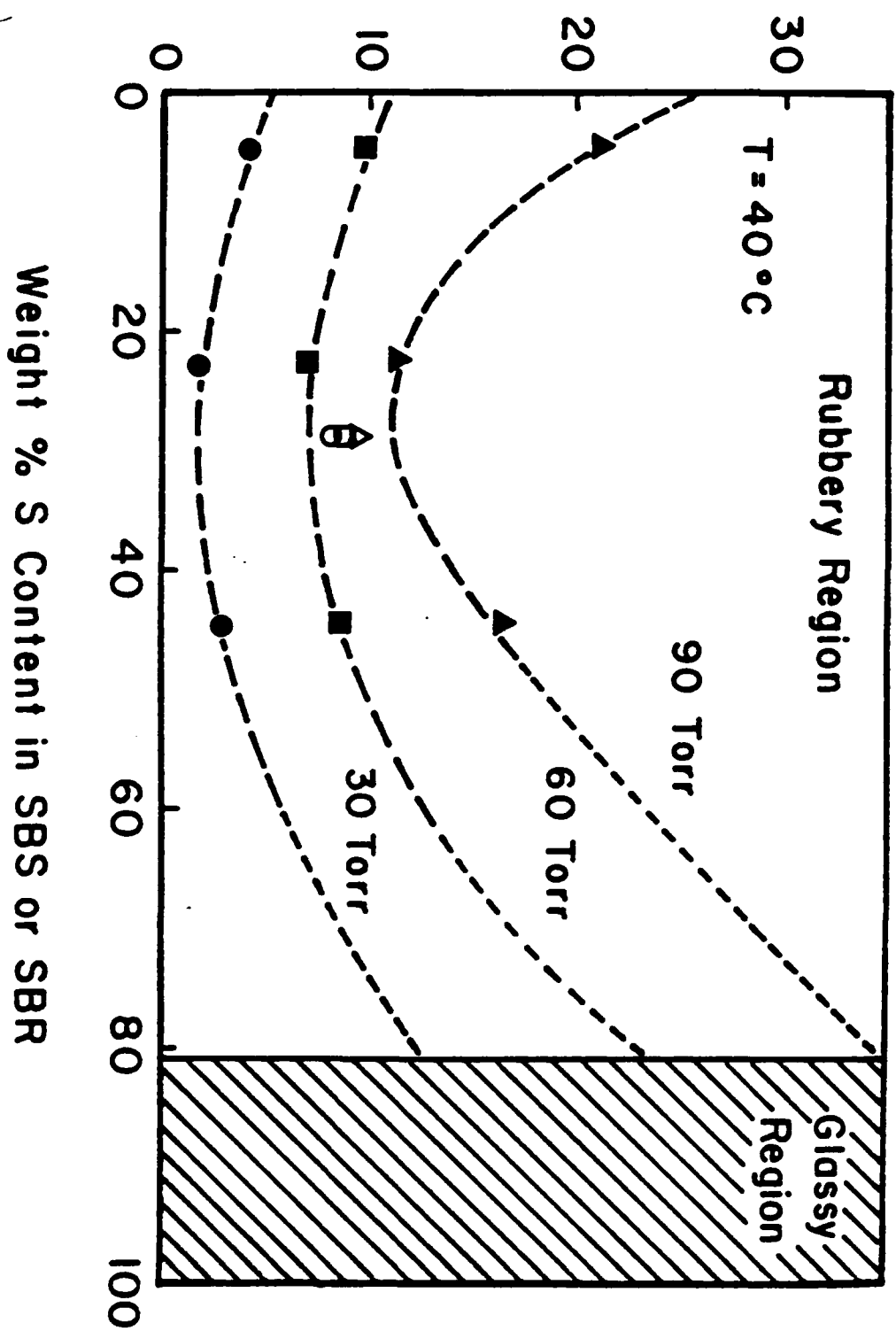
- Fig. 1 Apparatus for diffusion and sorption experiment.
- Fig. 2 Effect of penetrant activity,  $P/P_c$ , (relative pressure) on the equilibrium sorption of cyclohexane in SBR samples with 5, 23 and 45 weight % styrene content.
- Fig. 3 Equilibrium sorption of cyclohexane in SBS and SBR. Filled symbols are for SBR, whereas open symbols are for SBS. (a)  $\Delta$  : MEK/THF-cast samples; (b)  $\square$  : toluene-cast samples; and, (c)  $\circ$  : cyclohexane-cast samples.
- Fig. 4 Sorption and desorption curves at 40°C and 60 torr for cyclohexane in SBR.
- Fig. 5 Sorption and desorption curves at 40°C and 60 torr for cyclohexane in SBS cast from different solvents.
- Fig. 6 Sorption curves for cyclohexane in SBR (5, 23 and 45 wt % S content) samples at 40°C and 60 torr.
- Fig. 7 Sorption curves for cyclohexane in SBS at 40°C and 60 torr.
- Fig. 8 Effect of penetrant concentration on the mutual diffusion coefficient of cyclohexane in SBR at 40°C.



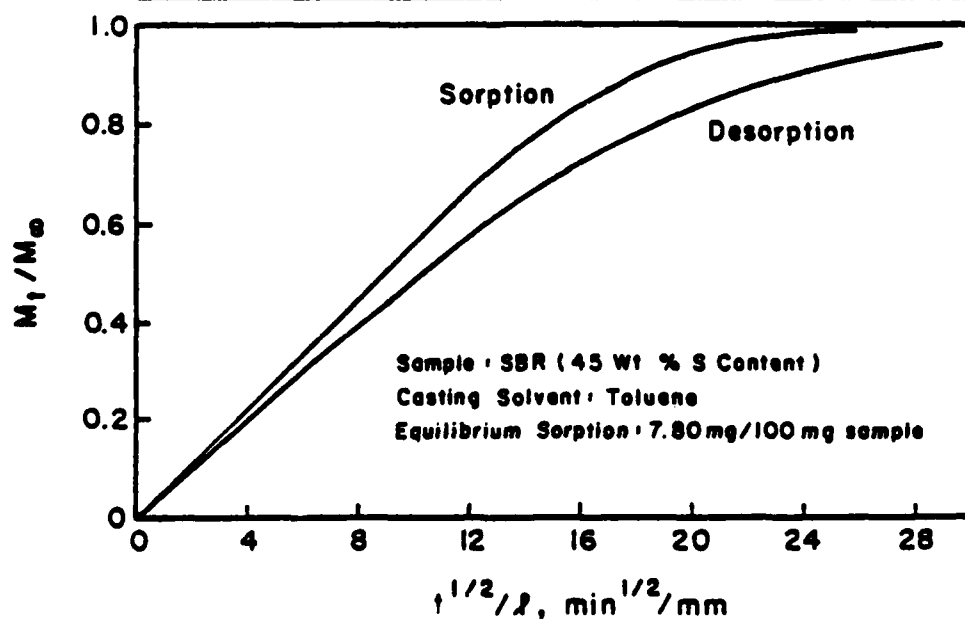
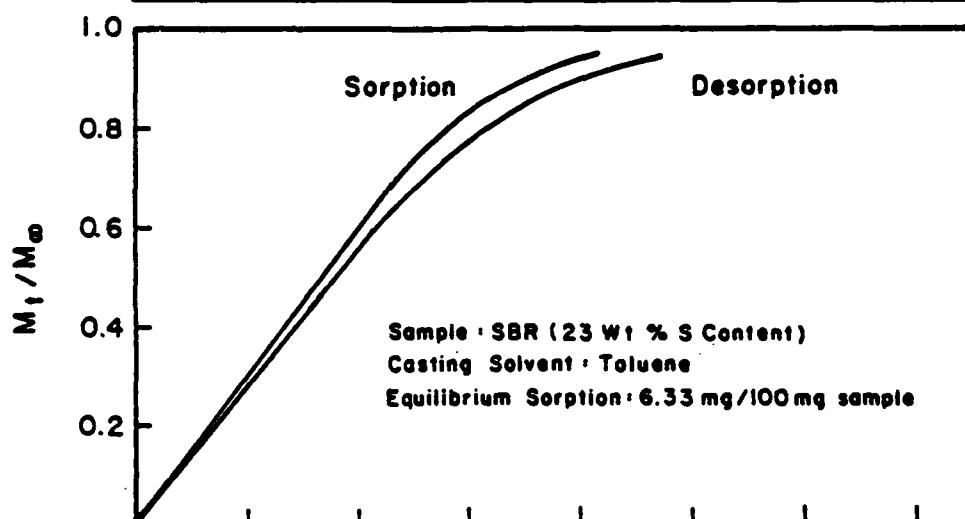
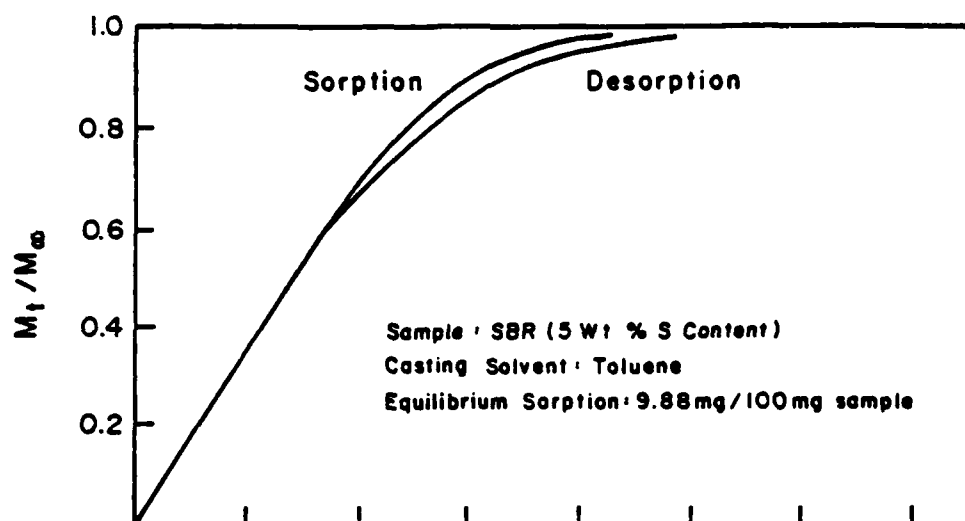
Equilibrium Sorption,  
mg / 100 mg sample

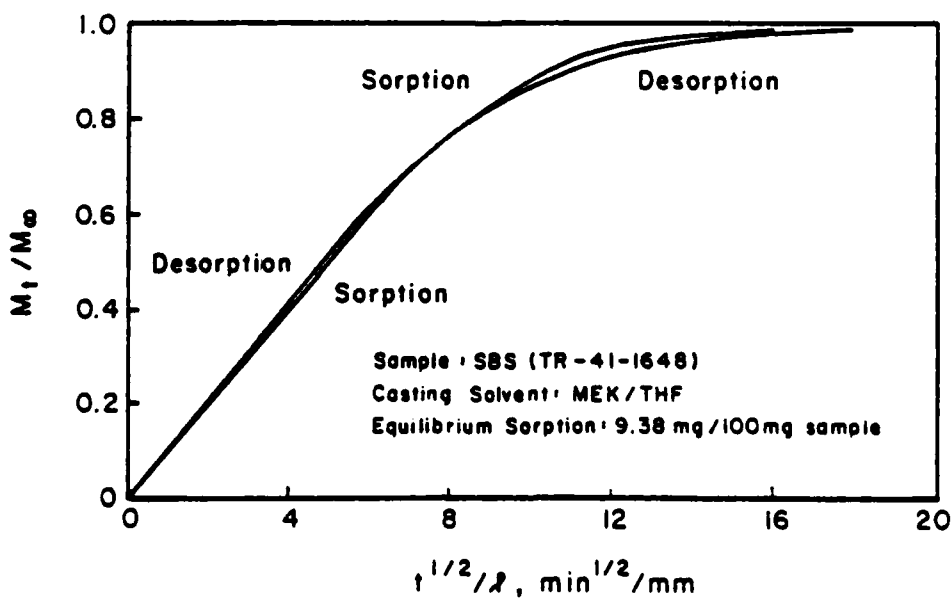
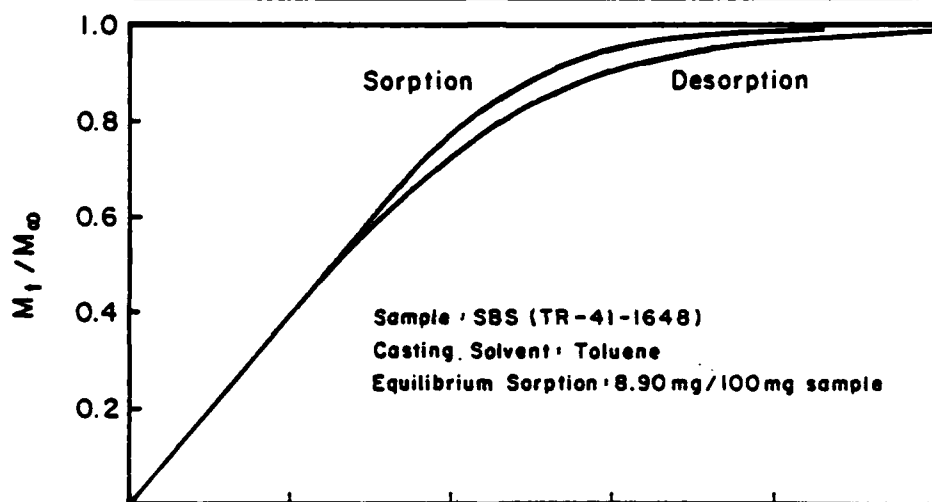
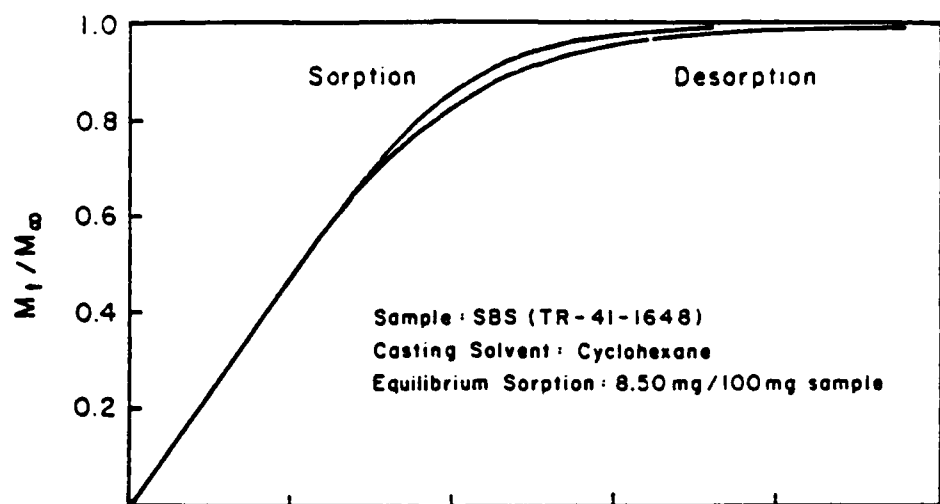


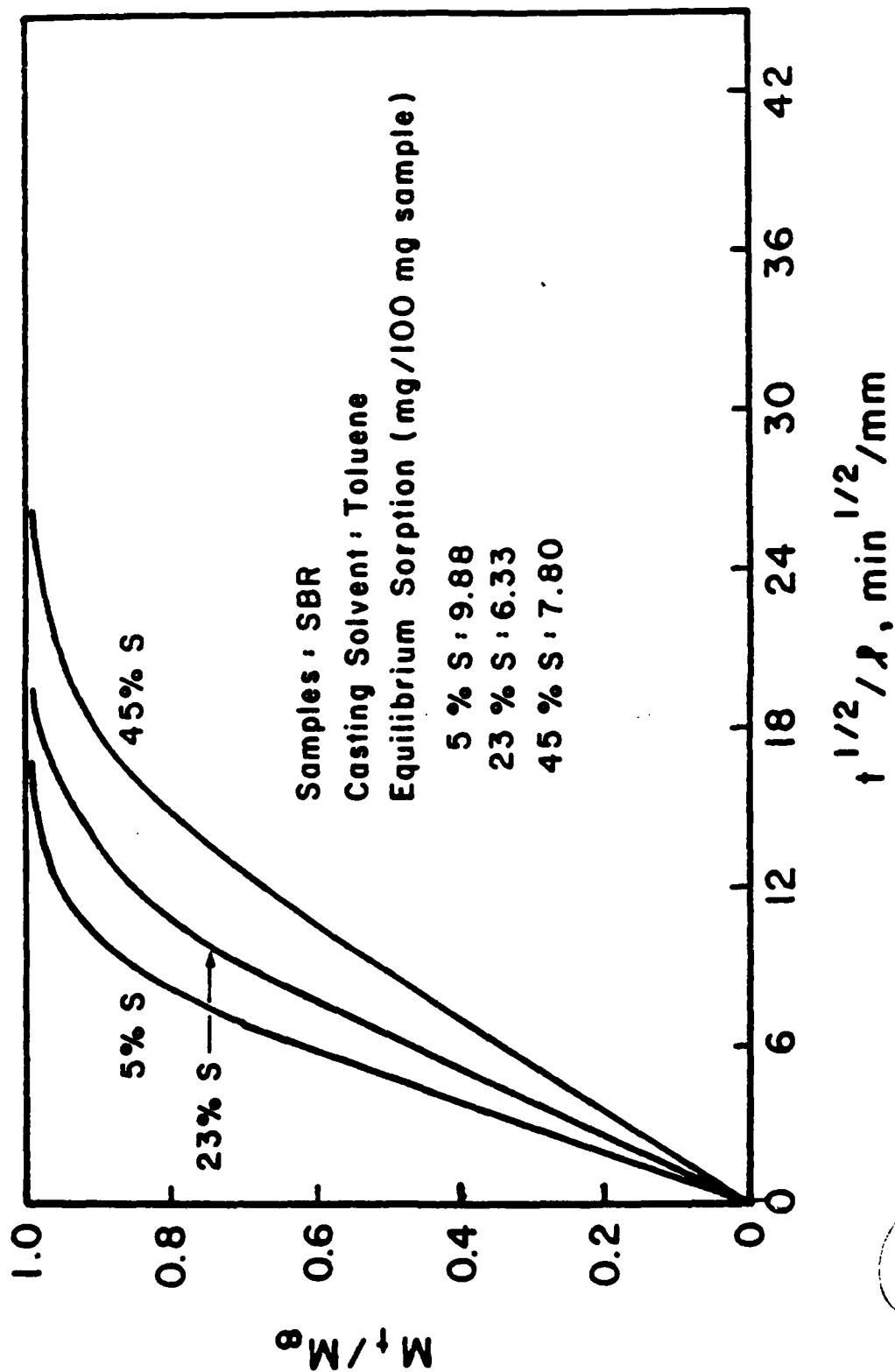
Equilibrium Sorption,  
mg / 100 mg sample

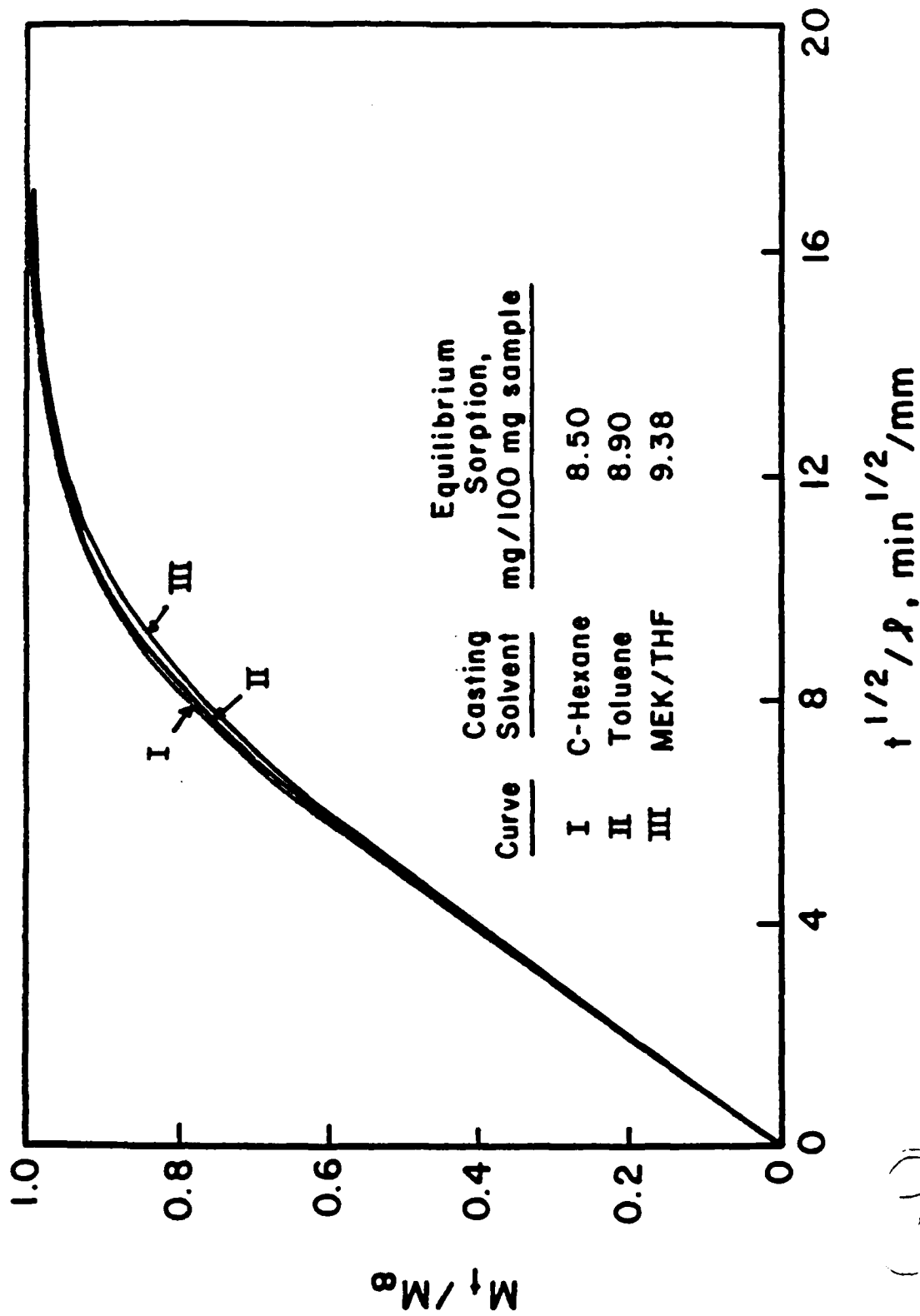


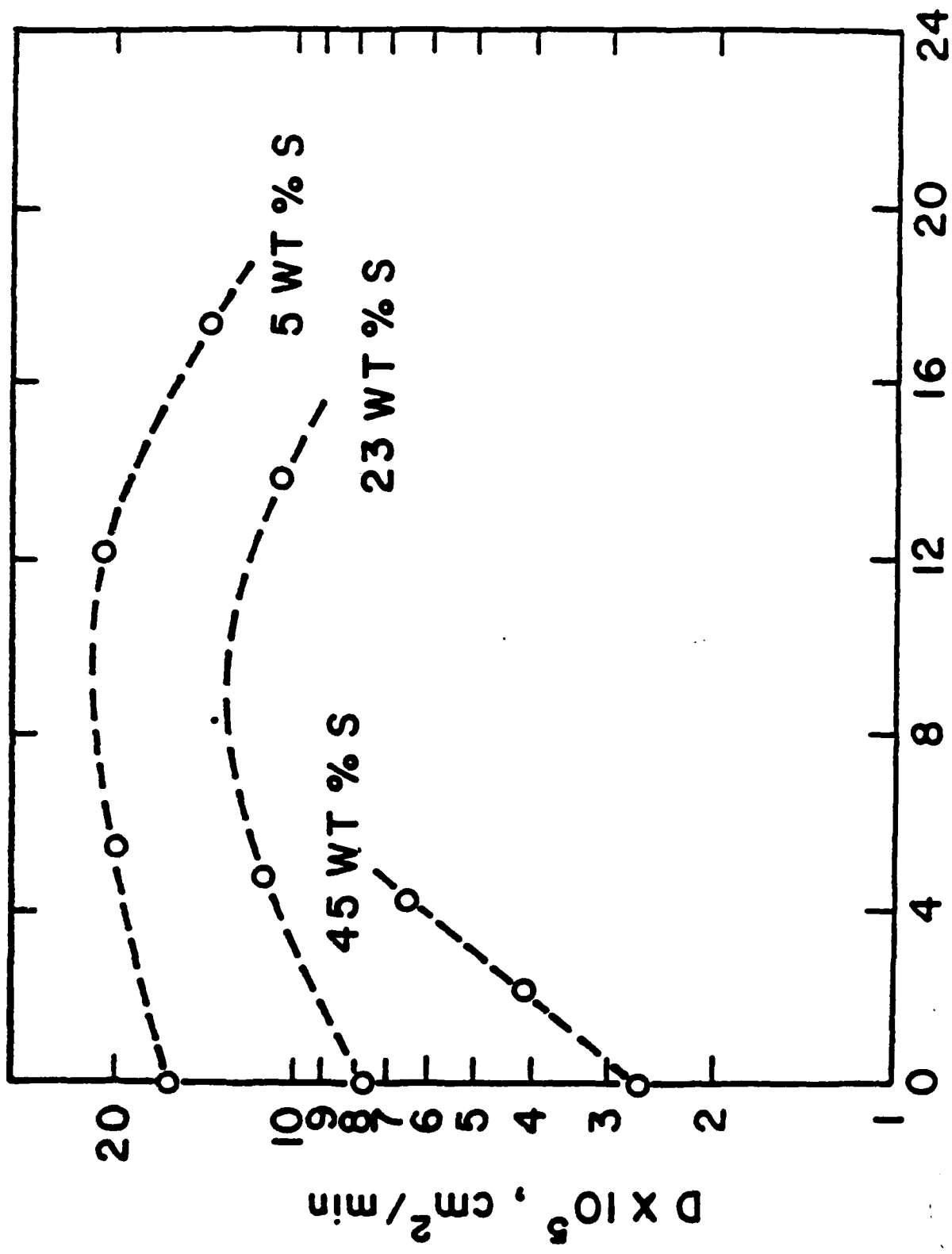












8 C, Moles Sorbed Cyclohexane / Total Volume (liter)

END

DATE  
FILMED

9 - 83

DT